Bulletin of Electrochemistry 1 (3) May-June 1985, pp. 267-270

CRYSTALLOGRAPHIC ORIENTATION OF ELECTRODEPOSITED LEAD DIOXIDE

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ABSTRACT

X-ray analyses on lead dioxide samples electrodeposited under different current densities from various concentrations of lead nitrate-copper nitrate solution, keeping the anode under stationary condition or rotation or under the influence of ultrasonic field, showed that the deposit of lead dioxide was only β – variety under all the experimental conditions studied. The ratio of lead-to-oxygen was determined in all the samples.

INTRODUCTION

Lead dioxide can be electrodeposited over suitable substrates to obtain a stable inert electrode [1-3]. In view of its high oxygen overvoltage, it is used as an anode in the production of sodium perchlorate as a replacement for platinum. In addition, lead dioxide anode finds application in the preparation of inorganic electrochemicals like halates [1,4-6], perhalates [1,7,8], certain organic electrochemicals [9], ozone [10-12] and in the purification of water [13]. The graphite substrate lead dioxide is used in the estimation of SO_2 from the atmosphere [14].

In the course of deposition of lead dioxide for use as anode, it may be of interest to know the crystallographic structure of lead dioxide under any particular conditions of electrolysis. Lead dioxide exists in two forms, namely, α-PbO_2 having orthorhombic structure (columbite) and β-PbO_2 with tetragonal structure (rutile) [15,16]. Pure forms of α and β-PbO_2 have been obtained both by chemical and electrochemical methods [17-21]. It has been reported by different authors [17-28] that solution pH, current density, Pb^{2+} concentration, anions present and temperature could play a vital role in deciding the crystallographic structure of electrodeposited lead dioxide. Lead dioxide has been deposited on platinum anode from pure lead nitrate solution [26], and after subjecting the samples to X-ray analysis, they were found to be either α or β-lead dioxide depending on the deposition conditions.

In order to study the effect of rotation [2-3] of the anode or the influence of ultrasonic field [29] on the polymorphs of lead dioxide, the same was deposited electrolytically from a mixture of lead nitrate – copper nitrate solution on a platinum anode kept either stationary, or rotating motion or under the influence of ultrasonic field. The samples obtained under different conditions were not only subjected to X-ray analysis but also analysed for lead-oxygen ratio and the results of the same are reported in this paper.

EXPERIMENTAL

Cell assembly

A 400 ml pyrex beaker fitted with a PVC cover containing suitable holes to introduce anode, cathode and thermometer was employed as cell container. A cylindrical perforated stainless steel (6 cm dia x 9.5 cm ht) was used as cathode and was fixed to the cell cover. A platinum tube fitted tightly into aluminium rod (1 cm dia x 10 cm ht) served as anode. The anode was kept either stationary or rotating or under the influence of ultrasonic field during deposition of lead dioxide.

When the anode was rotated, it was connected to the lower portion of the rotating shaft and electrical contact was given on the top through mercury placed in the cup. The speed of rotation was maintained at 1000 rpm. In the case of deposition under ultrasonic field [29], the cell assembly was suspended into the ultrasonic tank (45 Kc/s and 400 W) in such a way that the cell was not resting on the bottom of the tank. The tank was filled with water up to 3/4th capacity and its temperature was maintained by passing ice cold water through stainless steel coils kept in the tank.

Electrolysis

350 m*l* of the electrolyte containing lead nitrate (0.01 M to 1 M) and copper nitrate (0.1 M) was taken in the cell and the electrolysis was carried out by passing the same quantity of electricity for all the experiments and maintaining the temperature at 30 ± 1°C. Neutralisation of the acid in the electrolyte was carried out by adding calculated quantities of lead carbonate/lead monoxide and copper carbonate after removing the anode at the end of electrolysis. Samples were collected and analysed using the iodometric method [30] for determining the ratio of lead to oxygen. The same samples were subjected to X-ray analysis.

RESULTS AND DISCUSSION

Experiments were carried out using 1 M, 0.5 M, 0.1 M, 0.05 M and 0.01 M $Pb(NO_3)_2$ keeping the concentration of $Cu(NO_3)_2$ at 0.1 M. The current densities of 10, 5, 1 $A.dm^{-2}$ were employed, keeping the anode stationary or under rotating motion or under the influence of ultrasonic field. Under stationary condition, still lower current densities viz. 0.1, 0.05 and 0.01 $A.dm^{-2}$ were also employed. Typical results of X-ray analysis as well as lead-to-oxygen ratio are given in Tables I to III.

Table I: Structure and composition of lead dioxide deposited under stationary condition of the anode Temp: 30° C, pH = 4, Anode: platinum; copper nitrate = 0.1 M (fixed); Qty. of electricity = 3.2 A hrs.

No.	Concn. of $Pb(NO_3)_2$ (M)	Anode current density ($A.dm^{-2}$)	Lead-to-oxygen	Form of lead dioxide
1	2	3	4	5
1.	1	10	$PbO_{1.825}$	β-PbO_2. crystallinity poor
2.	"	5	$PbO_{1.94}$	β-PbO_2. Fairly good crystallinity
3.	"	1	$PbO_{1.952}$	β-PbO_2. "
4.	"	0.1	$PbO_{1.986}$	β-PbO_2 with traces of α-PbO_2 and red PbO as impurity
5.	"	0.05	$PbO_{1.928}$	do
6.	"	0.01	$PbO_{1.969}$	do
7.	0.5	10	$PbO_{1.93}$	β-PbO_2, less fine crystallinity
8.	"	5	$PbO_{1.922}$	do
9.	"	1	$PbO_{1.981}$	β-PbO_2. Fine
10.	"	0.1	$PbO_{1.903}$	β-PbO_2 with traces of α-PbO_2 and red PbO as impurity
11.	"	0.05	$PbO_{1.885}$	do
12.	0.1	10	$PbO_{1.936}$	β-PbO_2 of poor crystallinity
13.	"	5	$PbO_{1.95}$	β-PbO_2 with improved crystallinity
14.	"	1	$PbO_{1.95}$	do
15	"	0.1	$PbO_{1.953}$	β-PbO_2 with traces of α-PbO_2 and red PbO as impurity
16.	"	0.05	$PbO_{1.984}$	"
17.	0.05	10	$PbO_{1.990}$	Poor crystalline β-PbO_2.
18.	"	5	$PbO_{1.874}$	"
19.	"	1	$PbO_{1.815}$	β-PbO_2.
20.	"	0.1	$PbO_{1.921}$	β-PbO_2 with traces of α-PbO_2 and red PbO as impurity
21.	"	0.05	$PbO_{1.906}$	"
22.	0.01	10	–	β-PbO_2 with improved crystallinity
23.	"	5	$PbO_{1.921}$	β-PbO_2 with poor crystallinity
24.	"	1	$PbO_{1.92}$	"
25.	"	0.1	$PbO_{1.968}$	β-PbO_2 with traces of α-PbO_2 and red PbO as impurity
26.	"	0.05	$PbO_{1.969}$	"

Table II: Structure and composition of lead dioxide deposited under rotating conditions of the anode Temp: 30° C; pH = 4.0; Anode: platinum; copper nitrate = 0.1 M (fixed); Qty. of electricity = 3.2 A hrs; R.P.M = 1000.

No.	Conc. of $Pb(NO_3)_2$ (M)	Anode current density ($A.dm^{-2}$)	Lead-to-oxygen	Form of lead dioxide
1	1	10	$PbO_{1.886}$	β-PbO_2 improved crystallinity
2	"	5	$PbO_{1.926}$	β-PbO_2 "
3	"	1	$PbO_{1.923}$	β-PbO_2 with α-PbO_2 as impurity – fine
4	0.5	10	$PbO_{1.951}$	β-PbO_2, less fine crystallinity
5	"	5	$PbO_{1.928}$	"
6	"	1	$PbO_{1.935}$	β-PbO_2 with α-PbO_2 as impurity. Fine
7	0.1	10	$PbO_{1.95}$	β-PbO_2
8	"	5	$PbO_{1.96}$	"
9	"	1	$PbO_{1.972}$	β-PbO_2 with traces of α-PbO_2
10	0.05	10	$PbO_{1.971}$	Poor crystalline β-PbO_2
11	"	5	$PbO_{1.924}$	"
12	"	1	$PbO_{1.972}$	β-PbO_2 with traces of α-PbO_2
13	0.01	10	$PbO_{1.961}$	β-PbO_2 with poor crystallinity
14	"	5	$PbO_{1.942}$	"
15	"	1	$PbO_{1.951}$	β-PbO_2 with traces of α-PbO_2

Table III: Structure and composition of lead dioxide deposited under the influence of an ultrasonic field Temp: 30° C; Initial pH = 4.0; Anode: platinum; copper nitrate = 0.1 M (fixed); Qty. of electricity = 3.2 A hrs.

No.	Concn. of Pb $(NO_3)_2$ (M)	Anode current density ($A.dm^{-2}$)	Lead-to-oxygen	Form of lead oxide
1	2	3	4	5
1.	1	10	$PbO_{1.927}$	β-PbO_2 with traces of Pb_3O_4, improved crystallinity
2.	"	5	$PbO_{1.952}$	β-PbO_2; fine crystallinity
3.	"	1	$PbO_{1.938}$	β-PbO_2 with α-PbO_2 as impurity
4.	0.5	10	$PbO_{1.899}$	β-PbO_2, less fine crystallinity
5.	"	5	$PbO_{1.916}$	"
6.	"	1	$PbO_{1.953}$	β-PbO_2 with α-PbO_2 as impurity. Fine
7.	0.1	10	$PbO_{1.921}$	β-PbO_2 with improved crystallinity
8.	"	5	$PbO_{1.931}$	"
9.	"	1	$PbO_{1.961}$	β-PbO_2 with traces of α-PbO_2
10.	0.05	10	$PbO_{1.995}$	Poor crystalline β-PbO_2
11.	"	5	$PbO_{1.955}$	"
12.	"	1	$PbO_{1.965}$	β-PbO_2 with traces of α-PbO_2
13.	0.01	5	$PbO_{1.930}$	β-PbO_2 with poor crystallinity
14.	"	1	$PbO_{1.937}$	β-PbO_2 with good crystallinity

Studies on X-ray analysis show that the samples of lead dioxide are mainly β-variety under the conditions studied. However, it was seen that at low current densities (< 1 $A.dm^{-2}$), all the samples contained traces of α-lead dioxide as impurity. Pure β-lead dioxide was obtained at high current densities (≥ 5 $A.dm^{-2}$) at all concentrations studied, confirming earlier observations [26]. However, pure α-lead dioxide was not obtained in all the samples except in traces (as impurity only) along with β-form, though pure α-lead dioxide is claimed to have been obtained at low current densities (0.01 $A.dm^{-2}$) and high lead nitrate concentrations (150 – 300 g/l). Thus, it cannot be conclusively claimed that pure α-and β-lead dioxide can be obtained at roughly equal pH values by altering current density and concentration of electrolyte only.

The analytical results of the lead-to-oxygen content in most of the samples gave almost same values as reported earlier [31] for β-lead dioxide. The photomicrographs of the deposits of lead dioxide obtained on stationary and rotating anodes as well as under the influence of ultrasonics at a current density of 5 $A.dm^{-2}$ and a temperature of 30° C showed that while rotation of the anode and ultrasonic field gave a smooth deposit the deposit obtained on a stationary anode is coarse with pin holes.

Acknowledgement

The authors are thankful to the Director and Scientists of RRL, Jorhat, for providing the X-ray analysis data for all the lead dioxide samples.

REFERENCES

1. K C Narasimham and H V K Udupa, *J. Electrochem. Soc.* **123** (1976) 1294
2. K C Narasimham and H V K Udupa, *Proc. Symp. Electrolytic Cells*, CECRI Karaikudi (1961) p. 22
3. K C Narasimham, S Sundararajan and H V K Udupa, *J. Electrochem. Soc. Japan.* **29** (1961) 137
4. K C Narasimham, R Palanisami, M Sadagopalan, P D jose, P U John, V Rengarajan and H V K Udupa, *Proc. First Int. Symp. Industrial Electrochem.* Madras (1976) p. 67
5. S Pushpavanam, M Sadagopalan, K C Narasimham and H V K Udupa, Preprints *Second Int. Symp. Industry Oriented Basic Electrochem.* Madras (1980) p. 2.4
6. M S Venkatachalapathy, S Krishnan, M Ramachandran and H V K Udupa, *Electrochem. Technol.* **5** (1967) 399
7. H V K Udupa, K C Narasimham, M Nagalingam, N Thiagarajan, R Palanisamy, S Pushpavanam, M Sadagopalan, V Rengarajan, P D Jose and P U John, *Trans.* SAEST **13** (1978) 87
8. R Ramaswamy, M S Venkatachalapathy and H V K Udupa, *Indian. J. Tech.* **1** (1963) 115
9. K S Udupa, G S Subramanian and H V K Udupa, *Bull. Acad. Pol. Sci. Chim.* **9** (1961) 45
10. P C Foller and C W Tobias, *J. Electrochem. Soc.* **129** (1982) 506
11. P C Foller and C W Tobias, *J. Electrochem. Soc.* **129** (1982) 567.
12. J C G Thanos and D W Wabner, *J. Electroanal. Chem.* **182** (1985) 37
13. H C Miller and W Knipe, Electrochemical Treatment of Municipal Waste Water, U.S. Department of Health, Education and Welfare (1965) p. 18
14. P K Zutshi and T N Mahadevan, *Indian J. Environ. Health,* **17** (1975) 111.
15. R E Kirk and D R Othmer, *Encyclopedia of Chemical Technology,* Edn. 2, Vol. 12 Interscience, New York (1967) p. 276
16. C A Hampel, *Encyclopedia of Electrochemistry,* Reinhold Publishing Corporation, New York (1967) p. 763.

17. A J Bard (Ed), *Encyclopedia of Electrochemistry of the Elements,* Marcel Dekker Inc., New York (1973) p. 304

18. N E Bagshaw, R L Clarke and B Halliwell, *J. Appl. Chem.* **16** (1966), 180

19. J Burbank, A C Simon and E Willihnginz in P Delahay and C W Tobias (Eds) *Advances in Electrochemistry and Electrochemical Engineering,* Vol. 8, Interscience, New York (1971) p. 157

20. D Kordes, *Chem. Ing. Tech.* **38** (1966) 638.

21. W Mindt, *J. Electrochem. Soc.* **117** (1970) 615

22. D Fouque, P Foulloux, P Buisiare, D Weigell and M Prettre, *J. Chem. Phys.* **62** (1965) 1088

23. J P Carr and N A Hampson, *Chem. Rev.* **72** (1972) 679

24. J P Pohl and H Rickert, 'Electrochemistry of lead dioxide' in S Trasatti (Ed) *Electrodes of conductive metallic oxides,* Part A, Elsevier Scientific Publishing Co., New York (1980) pp. 183-220

25. R A Baker, *J. Electrochem. Soc.* **109** (1962) 337

26. A I Rusin, Z I Zhirilova, Yu M Shutova and K M Soloveva, *J. Appl. Chem. USSR,* **43** (1970) 337

27. J C G Thanos and D W Wabner, *J. Electroanal. Chem.* **182** (1985) 25

28. Ravi Varma, J Eckert, V A Maroni, J A Goldstone, C Giordano, T Cehelnik, Ramesh Kumar, Stantley Siegel and Ben Tani, *Electrochem. Soc.* Extended Abstracts, Fall 1984-2 Abstract No.4

29. K C Narasimham, P S Gomathi and H V K Udupa, *J. Appl. Electrochem.* **6** (1976) 397

30. A I Vogel, *A Text Book of Quantitative Inorganic Analysis including Elementary Instrumental Analysis,* 3rd Edn. Longmans Green and Co., London (1961) p. 358

31. P Ruetschi, R T Angstadt and B D Cahan, *J. Electrochem. Soc.* **106** (1959) 547.